98 Rec'd PCT/PTO 02 JAN 2002

FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER
217218US2PCT 10019278

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR
09/926847

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR00/01827	**29 June 2000**	**1 July 1999**

TITLE OF INVENTION
PROCESS AND DEVICE FOR DEPOSITING, BY ELECSTRON CYCLOTRON RESONANCE PLASMA, FILMS OF CARBON NANOFIBRE WEBS AND THE FILMS OF WEBS THUS OBTAINED

APPLICANT(S) FOR DO/EO/US
Marc DELAUNAY et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   - a. ☐ is attached hereto (required only if not communicated by the International Bureau)
   - b. ☒ has been communicated by the International Bureau.
   - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   - a. ☒ is attached hereto.
   - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   - b. ☐ have been communicated by the International Bureau.
   - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Notice of Priority/Form PTO-1449
PCT/IB/304/Drawings (4 sheets)
PCT/IB/308

PCTUS1/REV03

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U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 10/019278	INTERNATIONAL APPLICATION NO. PCT/FR00/01827	ATTORNEY'S DOCKET NUMBER 217218US2PCT

	CALCULATIONS	PTO USE ONLY
24. The following fees are submitted:.		
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :		
☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**		
☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**		
☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**		
☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**		
ENTER APPROPRIATE BASIC FEE AMOUNT =	**$890.00**	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$0.00**	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	30 - 20 =	10	x $18.00	**$180.00**	
Independent claims	3 - 3 =	0	x $84.00	**$0.00**	
Multiple Dependent Claims **(check if applicable).**			☐	**$0.00**	
TOTAL OF ABOVE CALCULATIONS =				**$1,070.00**	
☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				**$0.00**	
SUBTOTAL =				**$1,070.00**	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +				**$0.00**	
TOTAL NATIONAL FEE =				**$1,070.00**	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).**			☐	**$0.00**	
TOTAL FEES ENCLOSED =				**$1,070.00**	
				Amount to be: refunded	$
				charged	$

a. ☒ A check in the amount of **$1,070.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. ______________ in the amount of ______________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

22850

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Surinder Sachar
Registration No. 34,423

Surinder Sachar

SIGNATURE

Marvin J. Spivak

NAME

24,913

REGISTRATION NUMBER

Jan 2 2002

DATE

10/019278

217218US2-PCT 531 Rec'd PCT/PTC 02 JAN 2002

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :

MARC DELAUNAY ET AL : ATTN: APPLICATION DIVISION

SERIAL NO: NEW U.S. PCT APPLICATION :
(Based on PCT/FR00/01827)

FILED: HEREWITH :

FOR: PROCESS AND DEVICE FOR DEPOSITING, BY ELECTRON CYCLOTRON RESONANCE PLASMA, FILMS OF CARBON NANOFIBRE WEBS AND THE FILMS OF WEBS THUS OBTAINED :

10019278.020202

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to a first examination on the merits, please amend the above-identified application as follows:

IN THE CLAIMS

Please cancel Claims 1-26 without prejudice.

Please add new Claims 27-56 as follows:

27. (New) Process for depositing, by electron cyclotron resonance plasma, a web of carbons nanofibres or nanotubes onto a substrate without any catalyst, by injection of a microwave power into a deposition chamber comprising a magnetic structure with a highly unbalanced magnetic mirror and at least one electron cyclotron resonance zone within an interior of the deposition chamber itself and opposite the substrate, in which, under a pressure

less than 10^{-4} mbar, at least one of ionization and dissociation of a gas containing carbon is induced in the magnetic mirror in a center of the deposition chamber, thus producing species that deposit on the substrate, which is heated.

28. (New) Process according to claim 27, comprising the following steps:

heating the substrate;

establishing a pressure less than or equal to 10^{-4} mbar of a gas containing carbon;

injecting the microwave power, and creating the plasma from the gas containing carbon, for a value of the magnetic field corresponding to the electron cyclotron resonance;

creating a potential between the plasma and the substrate;

at least one of dissociating and ionizing molecules in the magnetic mirror at the center of the deposition chamber; and

depositing the species formed on the substrate in order to obtain a web of carbon nanofibres or nanotubes.

29. (New) Process according to claim 28, in which the steps are carried out simultaneously.

30. (New) Process according to claim 27, in which the deposited carbon is a graphite type carbon with a minority proportion of sp3 bonds and a majority proportion of sp2 bonds.

31. (New) Process according to claim 27, in which the structure of the magnetic mirror is such that a magnetic field is maximum (B_{max}) at microwave injection, the magnetic field is minimum (B_{min}) at the center of the deposition chamber, and the magnetic field increases on the substrate ($B_{substrate}$).

32. (New) Process according to claim 27, in which a mirror ratio upstream at the microwave injection, defined by $r_1 = B_{max}$ (in Gauss) / B_{min} (in Gauss), is greater than 4.

33. (New) Process according to claim 27, in which a mirror ratio, downstream towards the substrate, defined by $r_2 = B_{substrate}$ (in Gauss) / B_{min} (in Gauss), is greater than or equal to 1.5.

34. (New) Process according to claim 27, in which the substrate is heated to a temperature of 500 °C to 750 °C.

35. (New) Process according to claim 27, in which the pressure is less than or equal to $8x10^{-5}$ mbar.

36. (New) Process according to claim 27, in which the gas containing gas is chosen from methane, ethane, ethylene, acetylene, and their mixtures, possibly supplemented with hydrogen.

37. (New) Process according to claim 27, in which the heating of the substrate is achieved by electron bombardment or external heating.

38. (New) Process according to claim 27, in which the injection of the microwave power takes place at a frequency of 2.45 GHz.

39. (New) Process according to claim 27, in which the substrate is positively polarized, preferably from +20 volts to +100 volts, and the plasma is connected to a frame.

40. (New) Process according to claim 27, in which the plasma is negatively polarized, preferably from -20 to -100 volts, and the substrate is connected to a frame.

41. (New) Device for depositing, by electron cyclotron resonance (ECR) plasma, films of carbon nanofibre webs onto a substrate without a catalyst, the device comprising:

a deposition chamber;

means for creating a magnetic structure with a strongly unbalanced magnetic mirror in the deposition chamber;

an electron cyclotron resonance zone within an interior of the deposition chamber and opposite the substrate;

means for injecting a microwave power into the deposition chamber; and

means for creating a pressure less than 10^{-4} mbar of a gas containing carbon within the interior of the deposition chamber.

42. (New) Device according to claim 41, further comprising means for heating the substrate.

43. (New) Device according to claim 41, further comprising means for creating a potential difference between the plasma and the substrate.

44. (New) Film, which may be on the substrate, formed of a web or network of interconnected carbon nanofibres or nanotubes, like a spider's web, the film being free of any catalyst.

45. (New) Film according to claim 44, in which the carbon is a graphite type carbon with a minority proportion of sp3 bonds and a majority proportion of sp2 bonds.

46. (New) Film according to claim 44, in which the web or network has an average mesh size of from one or several tens of nm to one or several hundreds of nm, preferably from 20 to 200 nm.

47. (New) Film according to claim 44, in which the average diameter of the nanofibres or nanotubes is from one or several nm to one or several tens of nm, preferably from 1 to 100 nm.

48. (New) Structure with several layers - or multi-layer structures - comprising at least two layers of carbon nanofibre or nanotube webs according to claim 44.

49. (New) Filter comprising at least one film according to claim 44, which may be on a substrate.

50. (New) Filter according to claim 49, in which the film is spread out over a rigid grid with larger mesh size.

51. (New) Electron accelerating or decelerating nanogrid comprising at least one film according to claim 44.

52. (New) Flat screen, in particular with large dimensions, comprising a film according to claim 44, which may be on a substrate.

53. (New) Filter comprising at least one multi-layer structure according to claim 48, which may be on a substrate.

54. (New) Filter according to claim 53, in which the multi-layer structure is spread out over a rigid grid with larger mesh size.

55. (New) Electron accelerating or decelerating nanogrid comprising at least one multi-layer structure according to claim 48.

56. (New) Flat screen, in particular with large dimensions, comprising at least one multi-layer structure according to claim 48, which may be on a substrate.

IN THE ABSTRACT

Please amend the Abstract on page 34 as follows:

ABSTRACT OF THE DISCLOSURE

Process and device for depositing, by electron cyclotron resonance plasma, a web of carbon nanofibres or nanotubes, on a substrate without a catalyst, by injection of a microwave power into a deposition chamber including a magnetic structure with a highly unbalanced magnetic mirror and at least one electron cyclotron resonance zone within the interior of the deposition chamber itself and opposite the substrate. Under a pressure of less than 10^{-4} mbar, ionization and/or dissociation of a gas containing carbon is induced in the magnetic mirror in the center of the deposition chamber, thus producing species that deposit on the substrate, which is heated. A resulting film, which may be on a substrate, can be formed from a web or a network of interconnected carbon nanofibres or nanotubes, like a spider's web, the film being exempt of a catalyst and a structure of several layers - a multi-layer structure - including at least two layers of a web of carbon nanofibres or nanotubes, as well as filters, electron accelerating or decelerating nanogrids and flat screens including such films or structures.

REMARKS

Favorable consideration of this application, as presently amended, is respectfully requested.

The present Preliminary Amendment is submitted to place the above-identified application in more proper format under United States practice.

By the present Preliminary Amendment original Claims 1-26 are cancelled and new Claims 27-56 are presented for examination. New Claims 27-56 are deemed to be self-evident from the original disclosure, including the original claims, and thus are not deemed to raise any issues of new matter. Any differences between new Claims 27-56 and original Claims 1-26 are believed to at most broaden the scope of new Claims 27-56.

The Abstract has also been amended by the present response to delete legal phraseology, to be in the form of a single paragraph, and to make other minor clarifications.

The present application is believed to be in condition for a full and thorough examination on the merits. An early and favorable consideration of the present application is hereby respectfully requested.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
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53? ... 06 JAN 2002

Marked-Up Copy
Serial No:
____
Amendment Filed on:
1-2-2002

IN THE CLAIMS

Claims 1-26 (Cancelled).

Claims 27-56 (New).

IN THE ABSTRACT

Please amend the Abstract on page 34 as follows:

--ABSTRACT OF THE DISCLOSURE

Process and device for depositing, by electron cyclotron resonance plasma, a web of carbon nanofibres or nanotubes, on a substrate without a catalyst, by injection of a microwave power into a deposition chamber [comprising] including a magnetic structure with a highly unbalanced magnetic mirror and at least one electron cyclotron resonance zone within the interior of the [said] deposition chamber itself and opposite the [said] substrate[, in which, under]. Under a pressure of less than 10^{-4} mbar, [the] ionization and[ ]/[ ]or dissociation of a gas containing carbon is induced in the [said] magnetic mirror in the [centre] center of the deposition chamber, thus producing species that deposit on the [said] substrate, which is heated. A resulting film, which may be on a substrate, can be formed from a web or a network of interconnected carbon nanofibres or nanotubes, like a spider's web, the [said] film being exempt of a catalyst and a structure of several layers - a multi-layer structure - [comprising] including at least two layers of a web of carbon nanofibres or

nanotubes, as well as filters, electron accelerating or decelerating nanogrids and flat screens [comprising] <u>including</u> such films or structures.

[No figure.]--

PROCESS AND DEVICE FOR DEPOSITING, BY ELECTRON CYCLOTRON RESONANCE PLASMA, FILMS OF CARBON NANOFIBRE WEBS AND THE FILMS OF WEBS THUS OBTAINED

DESCRIPTION

The present invention concerns a process and a device for depositing, by electron cyclotron resonance plasma, films of carbon nanofibre webs.

In addition, the invention concerns the films of web obtained in this manner.

The technical field of the application may be defined, in a general manner, as that of depositing films of carbon on a substrate.

Such films are, in particular, films of carbon that emit electrons, but we have also sought to develop processes whose purpose is to synthesise films of diamond, and profitably employ the mechanical, optical and electrical properties of diamond at temperatures generally between 400 °C and 1 000 °C, or in order to make DLC ("Diamond Like Carbon") type carbon films, generally at low temperature (20 °C to 400 °C) and with a high level of C - C sp3 bonding, in particular for their mechanical properties.

Such films are principally amorphous.

More precisely, the present application is particularly concerned with the preparation of carbon films formed of nanotubes or nanofibres.

Table I, at the end of the description, shows different devices and processes for depositing, under vacuum, carbon films, used mainly for depositing emissive carbon.

This table highlights two different categories of deposition processes.

The first category involves CVD processes ("Chemical Vapour Deposition") in which a gas of organic molecules (often methane) is introduced as a mixture, with or without hydrogen, into a device that enables the C – C, C – H and H – H bonds to be broken by electron impact with, for example, the use of a hot filament, the introduction of microwave power, the use of a radio frequency (RF) polarisation or the use of an electron cyclotron resonance (ECR).

Depending on the device used, the operating pressure is either high (filament, microwave, radio frequency) or low (ECR, RF). The result is a dissociation and an ionisation of the particles, which increases as the pressure decreases. The energy that needs to be supplied for the reaction that transforms the gas into a solid is considerably decreased by the breaking of the covalent bonds (for example CH_4) of organic molecules.

It is thus possible to obtain graphite or diamond type crystallised structures at lower substrate temperatures (for example, 400 °C instead of 800 °C). The polarisation of the substrate also makes it possible to favour crystallisation at lower temperature, thus enabling the use of a wider variety of substrates.

The second category of deposition processes groups together the processes, called PVD processes (Physical Vapour Deposition), which involve the direct deposition of carbon atoms or ions, which may be achieved by spraying a graphite target by arc, by laser ablation, by a beam of ions or by evaporation.

The quality and the structure of the films, at a given temperature, mainly depend on the energy of the incident carbon ions or atoms.

In the case of the preparation of carbon nanotube or nanofibre films, which is of particular interest to us, within the scope of the present application, the PVD and CVD processes described above are also used.

Thus documents (18) and (19) concern processes for producing carbon nanotubes by PVD processes, with a direct supply of C° carbon atoms by laser ablation or electric arc. Document (18) describes, more precisely, a process for preparing carbon nanotubes using evaporation by arc between two graphite electrodes in helium, at high pressure (50 - 1 520 torrs). Binary mixtures of metals from the platinum group, such as rhodium and platinum, are used as catalysts.

The object of document (19) is the synthesis of tube type carbon structures in the form of pins by evaporation by arc discharging with a carbon electrode, within an enclosure filled with argon at 100 torrs.

The nanotubes or nanofibres can also be prepared by CVD processes, via catalytic de-hydrogenation of organic molecules such as acetylene or methane.

The device used may be make use of hot filaments, a radio frequency system or the injection of microwaves at high pressure, which generates atomic hydrogen and radicals or ions, such as CH_3^+, CH_3^0, CH^0, etc.

However, it should be pointed out that forming truly organised architectures of carbon nanofibres or nanotubes and not random and unorganised deposits has been explored up to now.

Thus, document (15) describes the synthesis of aligned carbon nanotubes using a process based on PECVD (Plasma Enhanced Chemical Vapour Deposition) of carbon from the decomposition of acetylene from a gaseous mixture of acetylene and nitrogen, with the deposition being catalysed by microparticles of iron imprisoned within the porous silica that forms the substrate.

Images obtained by scanning electron microscope show that the nanotubes are markedly perpendicular to the surface of the silica and form rows of tubes separated from each other by around 50 micrometers length and spaces of around 100 manometers.

Document (16) also describes the growth of orientated carbon nanotubes on monocrystalline and polycrystalline nickel substrates by the PECVD process, by using a hot filament. The carbon nanotubes have diameters of 10 to 500 nm and a length of 0.1 to 50 micrometers. Acetylene is used as the carbon source and ammonia is used as the diluting gas and for the catalysis.

Document (17) concerns the growth of films of carbon nanotubes on silicon substrates by CVD, from a mixture of methane and hydrogen, using a microwave plasma at a substrate temperature of 900 °C to 1 000 °C. Iron or nickel is deposited, beforehand, on the substrate in order to act as a catalytic seed for growing the nanotubes.

None of the processes described above allow organised architectures of carbon nanofibres or nanotubes to be made with strong bonds between the tubes in order to form a spider's web (2D structure).

We have seen that the alignment of the nanofibres or nanotubes could certainly be obtained (15) (16), but that, unless particular precautions are taken, the carbon nanotubes often develop (17) in a random unorganised manner, in the form of a jumble of filaments or spike structures without C – C bonds between the tubes (1D structure).

Although attempts, aiming to develop interconnections, have been carried out (18) by adding nanograins of catalyst, one again obtains, in this case, a disordered and random structure without strong C – C bonds between the tubes.

In addition, none of the processes described above allow films of nanotubes to be prepared and, moreover, organised architectures of carbon nanofibres or nanotubes, such as webs of nanofibres or nanotubes directly from organic molecules and without a catalyst.

Finally none of the processes allows the deposition of nanofibres or nanotubes over a large surface, in other words generally greater than or equal to 1 m^2.

There is therefore a need for a process for depositing webs of carbon nanofibres or nanotubes, not requiring a catalyst, which allows the deposition of such nano-architectures over large areas at a relatively low temperature.

The aim of the present invention is thus to provide a process for depositing webs of carbon nanofibres or nanotubes that meets, amongst other things, all of the requirements mentioned above.

The aim of the present invention is also to provide a process for depositing webs of carbon nanofibres or nanotubes that does not have the disadvantages, defects and limitations of the processes of the prior art and which resolve the problems of the prior art.

This aim and others are achieved, according to the present invention, by a process for depositing a web of carbon nanofibres or nanotubes onto a substrate by electron cyclotron resonance plasma, in the absence of a catalyst, by the injection of a microwave power into a deposition chamber comprising a magnetic structure with a highly unbalanced magnetic mirror, and at least one electronic cyclotron resonance zone within the said deposition chamber and opposite the said substrate, in which, at a pressure less than 10^{-4} mbar, the ionisation and / or the dissociation of a gas containing carbon is induced in the said magnetic mirror at the centre of the

deposition chamber, thus producing species that are deposited on the said substrate, which is heated.

More precisely, the said process comprises the following steps:

- Heating the substrate

- Establishing a pressure equal to or less than 10^{-4} mbar of a gas containing carbon

- Injecting microwave power, and creating a plasma from the said gas containing carbon, for a magnetic field value corresponding to the electron cyclotronic resonance

- Creating a potential difference between the plasma and the substrate

- Dissociating and / or ionising the molecules in the said magnetic mirror at the centre of the deposition chamber

- Depositing the species formed on the said substrate in order to obtain the webs of carbon nanofibres or nanotubes

In a particularly advantageous embodiment of the invention, the steps are carried out at the same time.

In fact, the process according to the invention can be placed between the two extreme processes, namely PVD (Physical Vapour Deposition) and CVD (Chemical Vapour Deposition), and it constitutes an excellent compromise between these two techniques, without having any of the disadvantages.

The process according to the invention meets the requirements mentioned above and resolves the problems of the processes of the prior art and, in particular, unlike

the processes for depositing nanofibres or nanotubes according to the prior art, the process according to the invention, which uses a specific ECR plasma, enables deposits to be formed on very large surfaces, greater than, for example, 1 m^2.

In the process according to the invention, a source of specific ECR plasma is used, which is a confining source, due to the implementation of a magnetic structure with a highly unbalanced magnetic mirror.

Furthermore, the ECR electronic cyclotron resonance zone, unlike most ECR plasma processes (20), is located, according to the invention, within the interior of the deposition chamber itself, opposite the substrate, and is thus integrated with it, and there is therefore no separation between the ECR plasma reaction chamber and the deposition chamber.

Then, in the process according to the invention, the said ECR plasma source, specific and confining, is used at very low pressure, generally less than 10^{-4} mbar.

It is essentially the combination of this specific and confining ECR plasma source with this very low pressure that makes it possible, in the process according to the invention, to strongly dissociate the organic molecules in order to obtain films formed from webs of carbon nanofibres or nanotubes, or networks of interconnected carbon nanofibres or tubes, as in a spider's web.

The ECR plasma, created according to the invention, is a stationary, stable plasma that, once installed,

persists and stabilises itself. Complete dissociation of the molecules is obtained, going up to the end of any possible dissociation. For example, methane can dissociate to give C° species.

More precisely, it can be said that it is the lifetime of the plasma particles that increases and not the lifetime of the plasma.

In other words, this notable magnetic confinement makes it possible to increase the lifetime of the ions and the electrons that remain trapped in the magnetic mirror at the centre of the deposition chamber and along the field lines. The level of dissociation and ionisation of the molecules in the plasma is thus increased with the following types of electron collisions:

$$CH_4 + e \rightarrow CH_3^+ + H^0 + e + e$$

$$CH_4 + e \rightarrow CH_3^0 + H^0 + e$$

$$CH^0 + e \rightarrow C^0 + H^0 + e, \text{ etc.}$$

The low pressure increases the energy of the electrons and reduces re-combination.

The deposited carbon is generally a graphite type carbon with a minority proportion of sp3 bonds and a majority proportion, for example greater than 80 %, of sp2 bonds.

In a surprising manner, according to the invention, it has been noted that for a pressure that does not conform with the invention, in other words a pressure greater than 10^{-4} mbar, there is practically no growth of

such carbon films but, on the other hand, the appearance of grains of graphite or diamond of various dimensions with, sometimes, cauliflower or lava cluster morphologies.

Films of carbon fibres, with the structure described above and without a catalyst, have never been obtained by the processes of the prior art.

Moreover, and according to an essential advantage of the process according to the invention, the structures of the web like films are obtained directly from an organic compound, without requiring a catalyst, such as a metal, for example nickel, cobalt or another metal.

The magnetic structure with a highly unbalanced magnetic mirror, according to the invention, is such that the magnetic filed is maximum (B_{max}) at the microwave injection, then the magnetic field is minimum (B_{min}) at the centre of the deposition chamber, and finally the magnetic field increases on the substrate ($B_{substrate}$).

In other words, it involves a strong magnetic mirror upstream at the injection and a weaker magnetic mirror downstream, in other words at the substrate level.

Advantageously, according to the invention the mirror ratio upstream, at the microwave injection, defined by $r_1 = B_{max} / B_{min}$ is greater than 4.

This high mirror ratio makes it possible to make ionised particles (ions and electrons) diffuse towards the substrate under the effect of a decreasing gradient.

Advantageously, the mirror ratio, downstream towards the substrate, defined by $r_2 = B_{substrate} / B_{min}$ is greater than or equal to 1.5, for example equal to around 1.5.

Preferably, according to the invention, the substrate is heated to a temperature of 500 °C to 750 °C, and preferably 550 °C to 700 °C, in order to provide the activation energy required for growth.

The substrate may be heated by electron bombardment or external heating; the electrons are those of the plasma, attracted by the substrate.

The substrate may be chosen from a wide variety of materials, whose deformation temperatures are greater than the operating temperature such as, for example, glass or silicon.

The substrate does not need to be a conductor. Whatever the case, it is the conductive carbon film that establishes the applied potential.

According to the invention, the pressure is maintained, preferably, at less than or equal to 8.10^{-5} mbar, in order to increase the energy of the electrons and reduce re-combination.

The gas containing carbon may contain carbon in any form whatever; any organic molecule is acceptable.

According to the invention, the gas containing carbon is, for example, methane, ethane, ethylene, acetylene and mixtures, possible supplemented with hydrogen, in any proportions.

Advantageously, the injection of the microwave power takes place at a frequency of 2.45 GHz, at a magnetic

field value of B, corresponding to the ECR, around 875 Gauss for a methane type gas.

Generally, the substrate is positively polarised, for example from + 20 volts to + 100 volts, with a flow of electrons that favours growth without a catalyst, in accordance with the invention, with the plasma connected to frame.

Another possibility consists in polarising the plasma negatively, for example from - 20 volts to - 100 volts, with the substrate connected to frame.

The invention also concerns a device for electron cyclotron resonance plasma deposition of films of carbon nanofibre webs onto a substrate free of any catalyst, the said device comprising:

- a deposition chamber
- the means for creating a magnetic structure with a highly unbalanced magnetic mirror in the said deposition chamber
- an electron cyclotron resonance zone within the interior of the said deposition chamber and opposite the said substrate
- the means for injecting a microwave power into the said deposition chamber
- the means for creating a pressure less than 10^{-4} mbar of a gas containing carbon within the interior of the said deposition chamber.

The device according to the invention may comprise, in addition, means for heating the substrate, if the

substrate is not sufficiently heated by the electrons of the plasma bombarding the substrate.

The device according to the invention may also comprise, in addition, the means for creating a potential difference between the plasma and the substrate.

As has already be pointed out, the device according to the invention stands out from ECR plasma devices of the prior art (20) mainly by the fact that there is no separation between the plasma creation chamber, the diffusion, and the deposition chamber, since the ECR zone is integrated within the deposition chamber.

The invention concerns, in addition, a film, which may be on a substrate, formed of a web or network of interconnected carbon nanofibres or nanotubes, like a spider's web, the said film being, moreover, free of any catalyst.

This type of web like film structure has never been obtained by processes of the prior art and may be prepared, for the first time, by the process of the invention without a catalyst, due to the use of a specific, confining ECR plasma source, and a low pressure of less than 10^{-4} mbar.

In other words, according to the invention, mono-architectures of carbon fibres or tubes are formed, which may be defined as webs ("nanowebs").

Unlike nanotubes created from catalytic nanograins, notably from metals, such as nickel, cobalt, etc., one obtains, according to the invention, without using any catalyst and, in a surprising manner, networks of

interconnected carbon nanofibres, such as in a spider's web.

The structure of the films according to the invention is an ordered fibrous structure and not a random, unordered structure, as with the prior art, where the films are, besides, polluted and contaminated by the catalyst.

"Free of catalyst" is taken to mean that the films, according to the invention, do not include elements that could be defined as catalysts, these elements being mainly metals, such as nickel, cobalt, iron, or that these elements are present in trace quantities or as normal impurities.

More precisely, the films according to the invention are made up of nanosegments of carbon linked between each other by strong carbon bonds, which constitutes a different morphology to the carbon nanofibre or nanotube structures of the prior art.

According to the invention, the deposited carbon is graphite type carbon with a minority proportion of sp3 bonds and a majority proportion of sp2 bonds, for example greater than 80 %.

"Nano-architecture" or "nanoweb" is generally taken to mean that the webs or networks of films according to the invention have an average mesh size of one or several tens of nm to several hundreds of nm, for example from 20 to 200 nm.

Preferably, the average mesh size is 100 nm.

In the same way, nanotubes or nanofibres is generally taken to mean that the diameter of the fibres or tubes is from one to several nm up to one or several tens of nm, for example from 1 to 100 nm, and preferably 20 nm.

The mesh size of the carbon fibre webs increases when the pressure of the gas, such as methane, is reduced, for example from 8.10^{-5} to 6.10^{-5} mbar.

The thickness of the films according to the invention is generally one or several nm to one or several tens of nm, for example from 1 to 100 nm.

The invention also concerns a structure with several layers (multi-layer structure) comprising at least two films of carbon nanofibre or nanotube webs according to the invention, which may be on a substrate.

This type of structure may comprise as many films as required by the application, and may have a thickness generally of from one or several tens of nm to one or several hundreds of nm, for example from 2 to 200 nm.

The structure on which the film or multi-layer structure described above is formed may be chosen from any of the substrates mentioned above; it could, for example, be glass, such a borosilicate glass or silicon.

It should be noted that, by extension, the films or structures according to the invention could also be called "webs".

The films according to the invention, formed from a web or network of carbon nanofibres or nanotubes have, in addition, apart from their specific structure, a certain

number of excellent properties, which make them particularly suitable for a wide range of applications.

The web or fibre of carbon according to the invention is an electrical conductor and refractory, like graphite.

Thus, it generally withstands temperature greater than 700 °C.

In addition, the mechanical strength of these films is excellent and these films are electron emitters under a field effect, at a field threshold of 10 to 20 V / µ.

Moreover, the films are chemically inert at ambient temperature, like graphite.

Finally, for the first time, large areas of films or multi-layer structures, for example from 0.25 m^2 to 1 m^2 may be formed according to the invention, and without the use of catalysts.

The properties described above may be used to good benefit in numerous possible applications of films and multi-layer structures according to the invention, formed from a web or network of interconnected carbon nanofibres or nanotubes, like in a spider's web.

The invention thus concerns a filter, in particular a bacterial filter, or a virus filter, comprising at least one of the said films or the said multi-layer structures, which may be on a substrate or on a grid.

In fact, the average mesh size of the carbon nanofibre webs according to the invention corresponds to the best known bacterial filters. For further details, the reader may refer to the work by G. LEYRAL, J.

FIGARELLA and M. TERRET, Microbiologie Appliqué, volume 2, J. LANORE publisher, p. 150 (liquids) and p. 174 (gases).

In particular, in the case of liquids, filters that can be used for the sterilised filtration of particles and bacteria whose size is greater than 0.2 μ can be made, 0.2 μ corresponding to the size of the smallest bacteria.

The filters according to the invention will therefore be defined as bacterial filters. For certain films, the filters according to the invention could filter viruses.

The films or multi-layer structures according to the invention may, in an advantageous manner, have a large surface. This property is particularly profitably employed in filtration, where large filtration surfaces have to be available for use.

In the filters according to the invention, the film or multi-layer structure is spread out on a rigid mesh, for example a metal mesh, with larger mesh size, for example several hundreds of μ, in order to allow filtration.

The invention also concerns electron accelerator or decelerator nanogrids comprising at least one film or at least one multi-layer structure according to the invention. The conductive and refractory properties of the films according to the invention are exploited in such nanogrids.

Moreover, the invention concerns a flat screen, in particular a large size flat screen, which comprises at least one film or at least one multi-layer structure according to the invention, which may be on a substrate. The fact that these films or structures emit electrons by field effect and can thus advantageously replace the metallic microdots presently used in flat screens may thus be exploited.

The applications given above are only some examples of the applications of the films and structures according to the invention, which may be applied in all fields where their properties, in particular their mechanical strength, may be profitably employed.

Brief description of the drawings

Figure 1 illustrates an electron cyclotron resonance plasma source with rectangular coils for the implementation of the process according to the invention, with the substrate advantageously unwinding along one dimension.

Figure 2 shows the profile of the axial magnetic field of the plasma source.

Figures 3A and 3B are photographs taken by a scanning electron microscope (SEM) of multi-layers of carbon nanofibre webs deposited on a silicon substrate by the process according to the invention. One graduation represents 1 μ.

Figures 4A and 4B are photographs taken by a scanning electron microscope (SEM) of multi-layers of carbon nanofibre webs deposited on a borosilicate glass substrate by the process according to the invention. One graduation represents 1 µ.

Figure 5 is a photograph taken by a scanning electron microscope (SEM) of a single layer of carbon nanofibres deposited on a borosilicate glass substrate by the process according to the invention. One graduation represents 100 nm.

In a more detailed manner, the process according to the invention may be implemented, for example, with the device as described in Figure 1.

This device comprises essentially a deposition chamber (1) in which there is a substrate (2).

This substrate (2) may be driven, for example, by a translational rectilinear displacement (3). The substrate (2) may be polarised, negatively, positively or connected to frame.

Preferably, the substrate is positively polarised, generally from + 20 to + 100 volts, as this type of positive polarisation makes it possible to complete the dissociation of the organic molecules on the substrate.

The substrate generally has a flat shape and a size of 0.25 m^2 to 1 m^2 which is, as has been seen, one of the advantages of the invention which allows films of carbon fibres to be deposited on relatively large surfaces, for example on substrates from 0.25 m^2 to 1 m^2 and more, which is particularly interesting for making large size flat

screens. The substrate is, for example, glass, such as a borosilicate type glass or silicon.

The substrate on which the films of carbon fibre are deposited may, also, preferably, be made out of a material that can be dissolved in an operation following the deposition operation, and the films of carbon fibre, thus separated from the initial substrate, are then spread out on a rigid mesh, for example, with larger mesh size, for example, made out of metal or alloy, such as tungsten or stainless steel, in the case where the web of carbon fibres is to be used as a bacterial filter.

The deposition chamber or enclosure (1) receives the power generated by one or several microwave emitters (arrow 13), via a coupler (4), which spreads out this power in the deposition chamber or enclosure.

This injection of microwave power into the enclosure produces the ionisation of a gas containing carbon under low pressure.

According to the invention, this low pressure is, as has already been indicated above, a pressure less than 10^{-4} mbar and preferably 8.10^{-5} mbar.

The low pressure within the deposition enclosure or chamber is maintained through pumping, represented by the arrow (5).

The gas containing carbon is, for its part, introduced upstream, in the coupler, for example via a pipe (6) fitted with an adjustment valve (7).

The gas is chosen, for example, from methane, ethane, ethylene, acetylene and their mixtures, possible mixed with hydrogen.

The coupler (4) comprises a microwave injection guide (8) ending in an elbow (9), which forms an angle of 90°, and which is connected to the deposition chamber or enclosure (1) perpendicular to it.

A microwave seal (10), for example made out of quartz, is placed in the wave guide between the admission wave guide (11) and the said 90° elbow (9).

This seal ensures the separation between the admission or injection guide (11) in which there is air at atmospheric pressure, and the elbow, as well as the deposition chamber or enclosure, which are under vacuum thanks to the pumping.

Due to the configuration described above, the microwave injection and the seal (10) are situated at 90° to the axis of the device, which makes it possible to avoid the seal being covered with carbon and ensures that the device operates in a continuous manner.

In accordance with the invention, the electron cyclotron resonance zone, represented by the reference (12) in Figure 1, is within the deposition chamber or enclosure itself and is opposite the substrate.

As a result, in the device of the invention, there is no separation between the plasma creation chamber (ECR), the diffusion and the deposition chamber, since, according to the invention, the ECR zone is integrated into the deposition chamber.

According to the invention, the microwave power is injected into a specific magnetic structure with a highly unbalanced magnetic mirror and comprising the electron cyclotron resonance zone (12), positioned as indicated above, within the deposition chamber (1) itself, which causes a dissociation and / or ionisation of the molecules making up the gas containing carbon, and produces species that are deposited on the said substrate.

The electron cyclotron resonance (ECR) magnetic field may be produced by conductor windings, such as coils or solenoids with a rectangular, square or cylindrical shape, or by permanent magnets.

In Figure 1, the magnetic field coils are rectangular magnetic field coils (14, 15, 16, 17).

The size of the deposition depends mainly on the area of the electron cyclotron resonance (ECR) magnetic field that is created. In the case of rectangular magnetic field coils (14, 15, 16, 17), shown in Figure 1, it is possible, for example, to obtain a plasma height of 25 cm, which can be extended to 1metre.

According to the invention, the magnetic field created has a particular shape, forming a magnetic structure with a highly unbalanced magnetic mirror. Thus, the shape of the axial magnetic filed created in the device in Figure 1 is represented in Figure 2, which gives the value of the axial magnetic field B (in Tesla) at various points located on the axis of the deposition

device; the abscissa represents a scale of length, with each graduation representing 10 cm.

In this figure, all of the vertical lines at the top of the graph represent the position of the rectangular magnetic field coils (14, 15, 16, 17) respectively supplied by currents of 370A, 370A, 900a and 900A.

In fact, according to the invention, it is the profile of the field that is important. To obtain this profile, the coils are supplied with currents in order to obtain the appropriate fields. For example, coils 14 and 15 are supplied with 370 A to give a field B = 600 G, and coils 16 and 17 are supplied with 900 A to give a field B = 2 700 G.

In this case, the desired ratios given above, i.e. $r_1 > 4$ and $r_2 > 1.5$, are indeed obtained.

On the curve representing the axial magnetic field are shown the positions of the deposition chamber, which is located between points A and B, the position of the substrate (point C), and the position of the electron cyclotron resonance (ECR) zone, represented by segment D. The arrow indicates the direction of the microwave injection and the injection of gas.

It can be seen that the magnetic field is at a maximum and high at the microwave injection, where it has a value, for example, of 2 700 G, the magnetic field is at a minimum, for example, of 600 G at the centre of the deposition chamber, and that the magnetic field then increases on the substrate.

One thus obtains a strong magnetic mirror at the injection point and a lower one downstream.

Typically, the injection mirror ratio r_1 is greater than 4.

Thus, in the case of the device shown in Figure 1, $r_1 = B_{max} / B_{min} = 2\,700\ G / 600\ G = 4.5$.

This high mirror ratio r_1 makes it possible to diffuse the ionised particles, ions and electrons, towards the substrate under the effect of the decreasing gradient.

Typically, the mirror ratio r_2 downstream, towards the substrate, is at least 1.5.

Thus, in the case of the device shown in Figure 1, $r_2 = B_{substrate} / B_{min} = 900\ G / 600\ G = 1.5$.

As has already been indicated above, the notable magnetic confinement, according to the invention, makes it possible to increase the lifetime of the ions and electrons, which remain trapped in the magnetic mirror at the centre of the deposition chamber and along the field lines.

The level of dissociation and ionisation of the molecules in the plasma are thus increased with the following types of electron collisions:

$$CH_4 + e \rightarrow CH_3^+ + H^0 + e + e$$

$$CH_4 + e \rightarrow CH_3^0 + H^0 + e$$

$$CH^0 + e \rightarrow C^0 + H^0 + e, \text{ etc.}$$

The invention will now be described, in referring to the following examples, which are given by way of indication and are in no way limiting.

Examples

According to the invention, nanowebs of carbon fibres or tubes are deposition on various substrates without any catalyst. The device used is more or less the same as that shown in Figure 1.

Example 1

In this example, the gas used is methane and the substrate is silicon heated to 640 °C.

The pressure within the deposition chamber or enclosure is 6.10^{-5} mbar.

In this way, multi-layers of a web or network of interconnected carbon nanofibres or nanotubes with a fibre diameter of around 20 nm are obtained, which are like a spider's web, and whose average mesh size is less than 200 nm.

Figures 3A and 3B are scanning electron microscope (SEM) photographs of such multi-layers.

We have also removed a film (single layer) from the multi-layer deposit and spread it out on the grid of a transmission electron microscope (TEM): this type of operation highlights the solidity of the films obtained by the process according to the invention. The

transmission electron microscope (TEM) photograph of the single layer is shown in Figure 5.

Example 2

In this example the gas used is methane and the substrate is borosilicate glass heated to 680 °C.

The pressure within the deposition chamber or enclosure is 8.10^{-5} mbar.

One thus obtains, in the same way as in Example 1, multi-layers of a web or network of interconnected carbon nanofibres or nanotubes with a fibre diameter of around 20 nm are obtained, which are like a spider's web, and whose average mesh size is near, or less than, 100 nm.

Figures 4A and 4B are scanning electron microscope (SEM) photographs of such multi-layers.

Apart from these SEM analyses and, if appropriate TEM analyses, other analyses may also be carried out. The results of all of the analyses carried out on the multi-layers or single layers in Example 1 and 2 are as follows:

- Composition: carbon (several % of hydrogen were identified) (determined by ERDA – Elastic Recoil Detection Analysis)

- TEM: diffraction photographs: the distance d (hkl) observed is 3.47 A, which corresponds more to a nanotube type structure (d = 3.44 A) than crystals of flat graphite (d = 3.35 A).

It should be noted that the nanotubes are rolled up and concentric films with hexagonal carbon cycles, as in graphite (whose films remain flat).

- SEM: multi-layers of nanoweb with a fibre diameter of around 20 nm (see Figures 3A, 3A, 4A and 4B).

- XPS (X-ray photoelectron spectroscopy): around 80 % of sp2 bonds (flat or rolled up graphite).

- Material that is a good electrical conductor like graphite

- X-ray analysis: graphite structure

- Raman spectroscopy (optical method with a laser): graphite structure.

- Temperature resistance: above 700 °C.

- Chemically inert at ambient temperature, like graphite.

Table I

Examples of carbon film deposits

	Device	Ref.	Process	Substrate temperature (°C)	Pressure (mbar)	% gas	Field threshold emission (V / µ)	Substrate polarisation (V)
DIAMOND	Hot filament	(1)	CVD (chemical vapour deposition)	800 to 1 000	30 to 50	1 % CH_4 / H_2	20	
DIAMOND	Microwave	(2)	CVD	800		1 % CH_4 / C_2H_5OH	22 to 50	
DIAMOND	Microwave	(3)	CVD	650 to 1 100	20 to 100	0.5 to 3 % CH_4		0 to − 300
DIAMOND	ECR	(4)	CVD	300 to 500	2×10^{-2} to 2	CH_3OH or 0.5 % CH_4		+ 30
DIAMOND	RF (or radio frequency)	(5)	CVD	700 to 1 200	20 to 30	0.2 to 1 % CH_4 / H_2		
DLC (Diamond like carbon)	Arc	(6)	C^+ ions	20	P ↓	Without	10	0 to − 350
DLC (Diamond like carbon)	RF	(7)	PECVD	20	10^{-3} to 3×10	CH_4 or 10 % CH_4 with He	5 to 20	− 100
DLC (Diamond like carbon)	Ion source	(8)	Bombardment of carbon by CO^+ ions	20			17	
DLC (Diamond like carbon)	Laser	(9)	Ablation → carbon plasma	20			10	
DLC (Diamond like carbon)	ECR	(10)	CVD	20 to 100	10^{-3} to 10^{-2}	20 % to 100 % CH_4		− 50 to − 500
Graphite	ECR	(11)	CVD	400 to 600	6×10^{-4}	CH_4 or 10 − 50 % H_2	10 to 30	+ 100
Graphite	Microwaves	(12)	CVD	800	40	1 % CH_4 99 % H_2	5	
Graphite	Soot	(13)	Soot bonding	20			20	
Graphite	Electrical discharge	(14)	CVD nanotubes	900		CH_4		

CLAIMS

1. Process for depositing, by electron cyclotron resonance plasma, a web of carbons nanofibres or nanotubes onto a substrate without any catalyst, by injection of a microwave power into a deposition chamber comprising a magnetic structure with a highly unbalanced magnetic mirror and at least one electron cyclotron resonance zone within the interior of the said deposition chamber itself and opposite the said substrate, in which, under a pressure less than 10^{-4} mbar, the ionisation and / or dissociation of a gas containing carbon is induced in the said magnetic mirror in the centre of the deposition chamber, thus producing species that deposit on the said substrate, which is heated.

2. Process according to claim 1, comprising the following steps:

- heating the substrate
- establishing a pressure less than or equal to 10^{-4} mbar of a gas containing carbon
- injecting the microwave power, and creating the plasma from the said gas containing carbon, for a value of the magnetic field corresponding to the electron cyclotron resonance
- creating a potential between the plasma and the substrate
- dissociating and / or ionising the molecules in the said magnetic mirror at the centre of the deposition chamber

- depositing the species formed on the said substrate in order to obtain a web of carbon nanofibres or nanotubes.

3. Process according to claim 2, in which the steps are carried out simultaneously.

4. Process according to any of claims 1 to 3, in which the deposited carbon is a graphite type carbon with a minority proportion of sp3 bonds and a majority proportion of sp2 bonds.

5. Process according to claim 1, in which the said structure of the magnetic mirror is such that the magnetic field is maximum (B_{max}) at the microwave injection, then the magnetic field is minimum (B_{min}) at the centre of the deposition chamber and finally the magnetic field increases on the substrate ($B_{substrate}$).

6. Process according to claim 1, in which the mirror ratio upstream at the microwave injection, defined by r_1 = B_{max} (in Gauss) / B_{min} (in Gauss) is greater than 4.

7. Process according to any of claims 1 to 6, in which the mirror ratio, downstream towards the substrate, defined by r_2 = $B_{substrate}$ (in Gauss) / B_{min} (in Gauss) is greater than or equal to 1.5.

8. Process according to any of claims 1 to 7, in which the substrate is heated to a temperature of 500 °C to 750 °C.

9. Process according to any of claims 1 to 8, in which the pressure is less than or equal to 8.10^{-5} mbar.

10. Process according to any of claims 1 to 9, in which the said gas containing gas is chosen from methane,

ethane, ethylene, acetylene, and their mixtures, possibly supplemented with hydrogen.

11. Process according to claim 1, in which the heating of the substrate is achieved by electron bombardment or external heating.

12. Process according to claim 1, in which the injection of the microwave power takes place at a frequency of 2.45 GHz.

13. Process according to claim 1, in which the substrate is positively polarised, for example from + 20 volts to + 100 volts, and the plasma is connected to frame.

14. Process according to claim 1, in which the plasma is negatively polarised, for example from - 20 to - 100 volts and the substrate is connected to frame.

15. Device for depositing, by electron cyclotron resonance (ECR) plasma, films of carbon nanofibre webs onto a substrate without a catalyst, the said device comprising:

- a deposition chamber
- the means for creating a magnetic structure with a strongly unbalanced magnetic mirror in the said deposition chamber
- an electron cyclotron resonance zone within the interior of the said deposition chamber and opposite the said substrate
- the means for injecting a microwave power into the said deposition chamber

- the means for creating a pressure less than 10^{-4} mbar of a gas containing carbon within the interior of the said deposition chamber

16. Device according to claim 15 comprising, in addition, the means for heating the substrate.

17. Device according to either of claims 15 and 16 comprising, in addition, the means for creating a potential difference between the plasma and the substrate.

18. Film, which may be on the substrate, formed of a web or network of interconnected carbon nanofibres or nanotubes, like a spider's web, the said film being free of any catalyst.

19. Film according to claim 18, in which the carbon is a graphite type carbon with a minority proportion of sp3 bonds and a majority proportion of sp2 bonds.

20. Film according to either of claims 18 or 19, in which the web or network has an average mesh size of from one or several tens of nm to one or several hundreds of nm, for example from 20 to 200 nm.

21. Film according to any of claims 18 to 20, in which the average diameter of the nanofibres or nanotubes is from one or several nm to one or several tens of nm, for example from 1 to 100 nm.

22. Structure with several layers - or multi-layer structures - comprising at least two layers of carbon nanofibre or nanotube webs according to any of claims 18 to 21.

23. Filter comprising at least one film according to any of claims 18 to 21 or at least one multi-layer structure according to claim 22, which may be on a substrate.

24. Filter according to claim 23, in which the said film or multi-layer structure is spread out over a rigid grid with larger mesh size.

25. Electron accelerating or decelerating nanogrid comprising at least one film according to any of claims 18 to 21, or at least one multi-layer structure according to claim 22.

26. Flat screen, in particular with large dimensions, comprising a film according to any of claims 18 to 21, or at least one multi-layer structure according to claim 22, which may be on a substrate.

ABSTRACT OF THE DISCLOSURE

Process and device for depositing, by electron cyclotron resonance plasma, a web of carbon nanofibres or nanotubes, on a substrate without a catalyst, by injection of a microwave power into a deposition chamber comprising a magnetic structure with a highly unbalanced magnetic mirror and at least one electron cyclotron resonance zone within the interior of the said deposition chamber itself and opposite the said substrate, in which, under a pressure of less than 10^{-4} mbar, the ionisation and / or dissociation of a gas containing carbon is induced in the said magnetic mirror in the centre of the deposition chamber, thus producing species that deposit on the said substrate, which is heated.

In addition, the inventions concerns a film, which may be on a substrate, formed from a web or a network of interconnected carbon nanofibres or nanotubes, like a spider's web, the said film being exempt of a catalyst and a structure of several layers - a multi-layer structure - comprising at least two layers of a web of carbon nanofibres or nanotubes, as well as filters, electron accelerating or decelerating nanogrids and flat screens comprising such films or structures.

No figure.

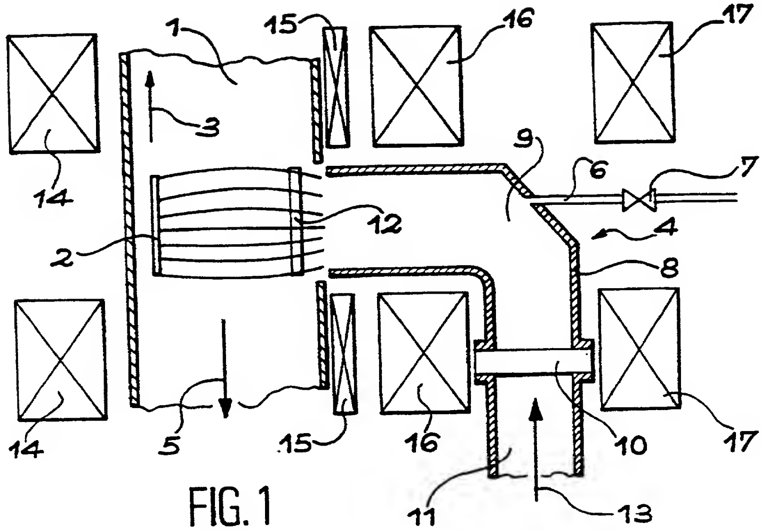
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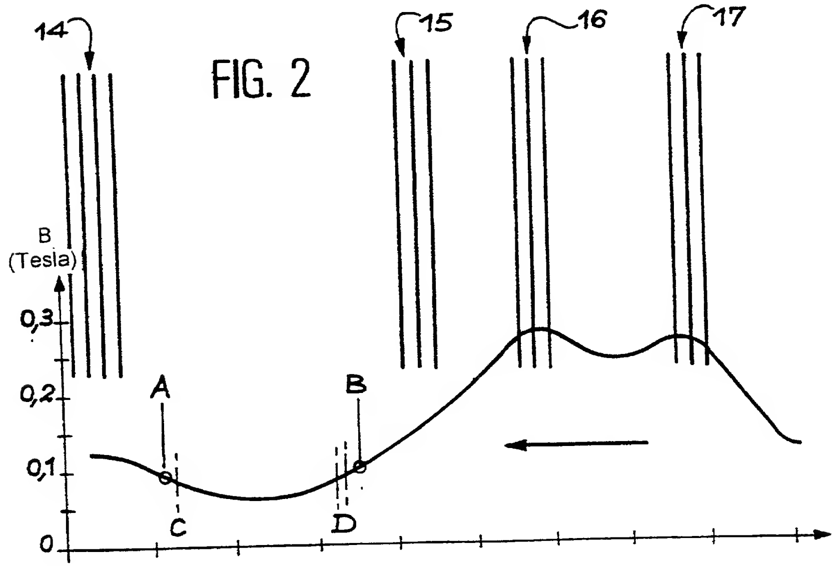
FIG. 1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(Tesla)
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0,2
0,1
0
A
B
C
D

FIG. 2

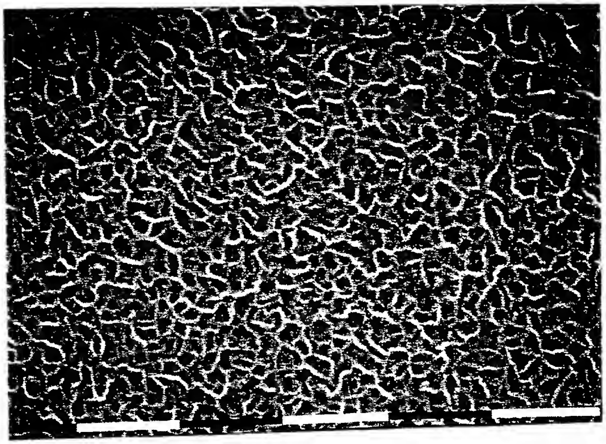


FIG. 3A

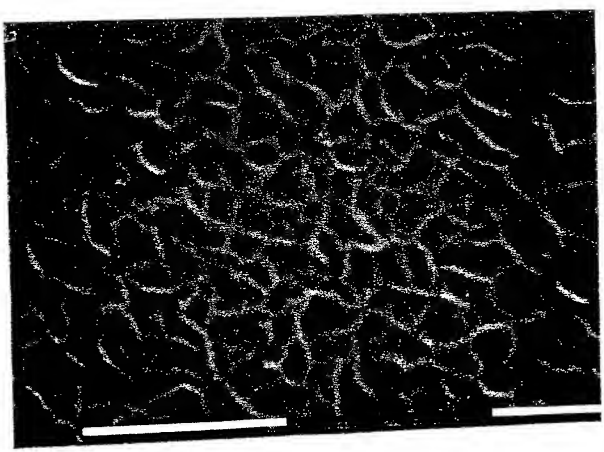


FIG. 3B

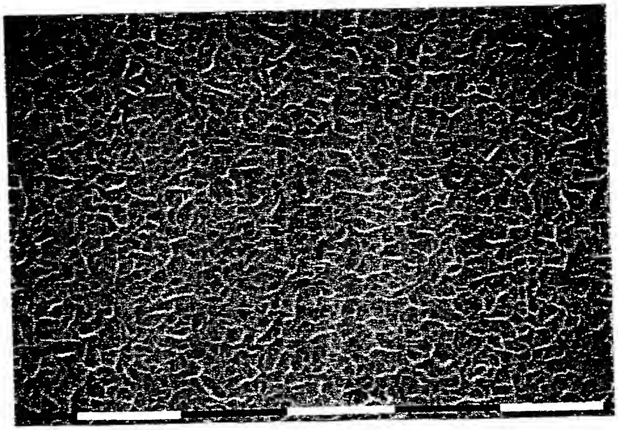


FIG. 4A

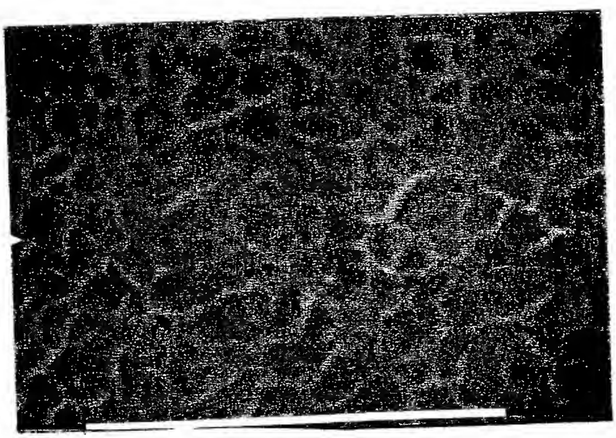
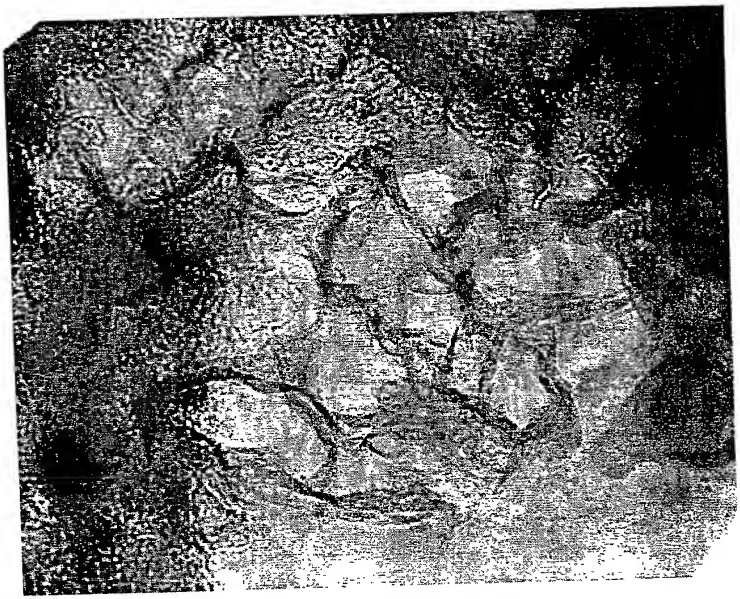


FIG. 4B



100 nm

FIG. 5

B 13307.3 PA

Declaration, Power Of Attorney and Petition

WE (I) the undersigned inventor(s), hereby declare(s) that :

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled
PROCESS AND DEVICE FOR DEPOSITING, BY ELECTRON CYCLOTRON RESONANCE PLASMA, FILMS OF CARBON NANOFIBRE WEBS AND THE FILMS OF WEBS THUS OBTAINED

the specification of which

☐ is attached hereto.

☐ was filed on

as Application Serial No.

and amended on

☒ was filed as PCT international application

Number PCT/FR00/01827

on June 29, 2000

and was amended under PCT Article 19

on

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365 (a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application (s)

Application No.	Country	Day/month/Year	Priority Claimed
99 08473	FRANCE	01 JULY 1999	☒ YES ☐ NO
			☐ YES ☐ NO
			☐ YES ☐ NO
			☐ YES ☐ NO

We (I) hereby claim the benefit under Title 35, United States Code, § 119 (e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)

And we (I) hereby appoint : Norman F. Oblon, Registration Number 24,618; Marvin J. Spivak, Registration Number 24,913; C. Irvin McClelland, Registration Number 21,214; Gregory J. Maier, Registration Number 25,599; Arthur I. Neustadt, Registration Number 24,854; Richard D. Kelly, Registration Number 27,757; James D. Hamilton, Registration Number 28,421; Eckhard H. Kuesters, Registration Number 28,870; Robert T. Pous, Registration Number 29,099; Charles L. Gholz, Registration Number 26,395; Vincent J. Sunderdick, Registration Number 29,004; William E. Beaumont, Registration Number 30,996; Steven B. Kelber, Registration Number 30,073; Robert F. Gnuse, Registration Number 27,295; Jean-Paul Lavalleye, Registration Number 31,451; William B. Walker, Registration Number 22,498; Timothy R. Schwartz, Registration Number 32,171; Stephen G. Baxter, Registration Number 32,884; Martin M.,. Zoltick, Registration Number 35,745; Robert W. Hahl, Registration Number 33,893; and Richard L. Treanor, Registration Number 36,379; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P.C., whose post Office Address is : Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true ; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardise the validity of the application or any patent issuing thereon.

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☒ ***Scanned copy is best available.*** Drawings fig 3A, 3B, 4A, 4B, and fig5 are very dark.